

1. For the reactions below at pH 7 and 25°C the standard half cell voltages are:  
 $2H^+ + 1/2 O_2 + 2e^- \rightarrow H_2O$   $E^{\circ'} = 0.820 \text{ V}$  and  
 $2H^+ + \text{cystine} + 2e^- \rightarrow 2 \text{ cysteine}$   $E^{\circ'} = -0.340 \text{ V}$ .

a) Write the balanced reaction which will be spontaneous when these half cells are connected. If the second half cell is made with 0.01 M cystine and 0.01M cysteine both present, what will be cell the potential and  $\Delta G$  for the overall reaction under these conditions?



$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{0.01}{0.01} = 1.160 - 0.0591 = 1.1009$$

- b) The cell voltage was also measured at 45°C, and the cell potential was found to have decreased relative to 25°C by 0.0121V. What are the values of  $\Delta H$  and  $\Delta S$  for the reactions in the cell?

$$\text{need } \frac{\partial E}{\partial T} = \frac{\Delta E}{\Delta T} = \frac{-0.0121 \text{ V}}{20^\circ \text{K}} = -6.05 \times 10^{-4}$$

$$\Delta S = 96,485 \text{ n } \frac{dE}{dT}$$

$$\Delta S = -116.7 \text{ J/K}$$

$$\Delta H = 96,485 \text{ n } \left( -E + T \frac{dE}{dT} \right) = -247 \text{ kJ}$$

25°C

= 298 K

- c) If the pH in both half cells was decreased by two units would the cell potential increase or decrease (why)? If the pH in just the cystine/cysteine half cell were decreased what would happen?

If pH is the same then in Q  $[H^+]$  cancels  
 so cell voltage is the same.

$H^+$  is a product in the second half cell,  
 so  $[H^+]$  of that cell is in the ~~numerator~~ denominator

pH  $\uparrow$  means  $[H^+]$  up so Q larger

so E decreases

3. A galvanic cell is made at 25°C with 1M solutions of  $\text{Fe}^{+3}$  and  $\text{Fe}^{+2}$  with a platinum electrode on one side, and a saturated solution of  $\text{AgCl}$  with a  $\text{Ag}$  electrode on the other side.  $\text{AgCl}$  has a solubility product of  $1.8 \times 10^{-10}$  at 25°C.

a) Use the data above and that in Table 4.5 to calculate the cell voltage which would be measured.

$$[\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10} \quad [\text{Ag}^+] = 1.342 \times 10^{-5}$$

$$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad 0.771$$

$$\text{Ag}^+ + e^- \rightarrow \text{Ag} \quad 0.799$$

$$\varepsilon = \varepsilon^\circ - \frac{0.0591}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}][\text{Ag}^+]}$$

$$\text{Ag}^+ + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Ag} \quad \varepsilon^\circ = 0.028\text{V} \quad \begin{matrix} 0.018\text{V} - 0.288 \\ = -0.2595\text{V} \end{matrix}$$

b) If 0.01 M  $\text{NaClO}_4$  is added to the silver side (assume  $\text{Na}$  and  $\text{AgClO}_4$  are soluble and that perchlorate is nonreactive), what will be the change in the cell potential?

ionic strength effects  $\text{Ag}^+$  solubility will change

$I = 0.01$  (can ignore  $\text{Ag}^+$  &  $\text{Cl}^-$ )

$$\log \gamma_{\pm} = -0.509 \cdot |+1 \cdot -1| \sqrt{0.01} = -0.0509$$

$$\gamma_{\pm} = 0.889$$

$$K_{sp} = \gamma^2 \cdot [\text{Ag}^+][\text{Cl}^-] \quad \text{so} \quad [\text{Ag}^+] = 1.509 \times 10^{-5} \quad \text{so} \quad V = -0.257$$

c) When  $\text{NH}_3$  is added to  $\text{AgCl}$  it dissolves to form  $\text{Ag}(\text{NH}_3)_2^+$ . If  $\text{NH}_3$  is added to the silver half cell in which direction would you expect the cell voltage to change if at all (explain your answer)?

since  $\text{AgCl}$  dissolves, the stability constant of  $\text{Ag}(\text{NH}_3)_2^+$  must be higher, free  $[\text{Ag}^+]$  is lower so voltage will be lower.